

REMARKS

This preliminary amendment is being filed concurrently with Applicants' application LU 6132 (US), for which a serial number has not yet been assigned.

The specification has been amended to insert a reference to the corresponding International Application and priority documents. A substitute specification is submitted with this Amendment, along with markings showing all the changes. A clean version of the specification, without markings, is also included with this Amendment. Claims 1-10 have been amended to put them in better form. No new matter has been added by these amendments and they do not affect the scope of the claims as originally filed.

It is not believed that any fee is required for entry and consideration of this Amendment; nevertheless, the Commissioner is hereby authorized to charge U.S. PTO Deposit Account 08-2336 in the amount of any such required fee.

Respectfully submitted,

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LU6132

ATTACHMENT A

SUBSTITUTE SPECIFICATION
WITH MARKINGS SHOWING ALL CHANGES

5 LOOP REACTOR WITH VARYING DIAMETER FOR OLEFIN POLYMERIZATIONS

This application is the U.S. national phase of International Application PCT/EP2004/010375, filed 10 September 16, 2004, claiming priority to German Patent Application 10344500.5 filed Septemer 24, 2003, and the benefit under 35 U.S.C. 119(e) of U.S. Provisional Application No. 60/529,037, filed December 12, 2003; 15 the disclosures of International Application PCT/EP2004/010375, German Patent Application 10344500.5 and U.S. Provisional Application No. 60/529,037, each as filed, are incorporated herein by reference.

The present invention relates to a process for 20 polymerizing at least one olefinic monomer in a loop reactor at from 20 to 150°C, but below the melting point of the polymer to be formed, and a pressure of from 5 to 100 bar, where the polymer formed is present in a suspension in a liquid or supercritical suspension 25 medium and this suspension is circulated by means of an axial pump.

The present invention further provides a loop reactor for the polymerization of olefinic monomers which 30 comprises a cyclic reactor tube and an axial pump, particularly an impeller pump for conveying the polymerization mixture.

Suspension polymerization processes for polymerizing 35 olefins have been known for a long time. A suspension polymerization in which the polymerization is carried out in a loop reactor has been found to be particularly

useful for the polymerization of ethylene in particular, usually together with further comonomers. In such loop reactors, the polymerization mixture is pumped continuously through a cyclic reactor tube. The 5 pumped circulation firstly achieves continual mixing of the reaction mixture, and also distributes the catalyst metered in and the feed monomers in the reaction mixture. Secondly, the pumped circulation prevents sedimentation of the suspended polymer. The removal of 10 the heat of reaction via the reactor wall is also promoted by the pumped circulation.

The polymer is generally discharged from the loop reactor in a discontinuous fashion in sedimentation 15 legs. These sedimentation legs are projections which branch off vertically from the lower part of the reactor tube and in which the polymer particles can settle. After sedimentation of the polymer has reached a particular point, a valve at the lower end of the 20 sedimentation legs is opened briefly and the polymer which has settled is discharged discontinuously.

Since loop reactors have been used for production purposes for many years, numerous efforts have been 25 made to improve the economics of these reactors and the polymerization processes carried out therein. An increase in the space-time yield of the process is particularly desirable. The space-time yield is, in particular, limited by removal of the heat of reaction 30 via the reactor wall and by the polymer content of the reaction suspension. An increase in the proportion of solids in the reactor will, in particular, make discharge of the polymer more effective and increase the mean residence time of the polymer in the reactor.

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US-A-6,239,235 describes a polymerization process in a loop reactor, in which an increase in the average proportion of solids in the reactor is achieved by

means of a continuous discharge system. This continuous discharge system was able to achieve an average proportion of solids in the reactor of 53% by weight, whereas the conventional discontinuous discharge
5 achieved an average solids concentration of only 45% by weight. In accordance with conventional teachings, the document makes no reference to a varying reactor diameter; in contrast, disturbance-free flow is said to be achieved by means of gentle curves. Only in the
10 region of the impeller pump does there seem to be, apparently for reasons of impeller construction, a short widening of the reaction tube diameter. The process described in this document, too, leaves something to be desired in respect of the solids
15 concentration in the reactor. The document also confirms the prevailing view that it is generally not possible to achieve polymer solids concentrations of more than 37-40 percent by weight in suspension polymerization processes.

20 It is an object of the present invention to find a process for polymerizing olefinic monomers in a loop reactor, which process makes higher solids concentration in the reactor and higher space-time
25 yields possible.

We have found that this object is achieved by the process described at the outset when the loop reactor used comprises a cyclic reactor tube whose diameter
30 varies by at least 10%, based on the predominant reactor tube diameter, and in which there is at least one widening and narrowing in a region other than that of the axial pump.

35 In addition, we have found a process for polymerizing at least one olefinic monomer in a loop reactor at from 20 to 150°C, but below the melting point of the polymer to be formed, and a pressure of from 5 to 100 bar,

wherein the polymerization is carried out at an average solids concentration in the reactor of more than 53% by weight, based on the total mass of the contents of the reactor.

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The achievable solids concentration can depend on whether product discharge is continuous or discontinuous. We have accordingly found a process for polymerizing at least one olefinic monomer in a loop 10 reactor at from 20 to 150°C, but below the melting point of the polymer to be formed, and a pressure of from 5 to 100 bar, wherein the polymerization is carried out at an average solids concentration in the reactor of more than 53% by weight, based on the total 15 mass of the contents of the reactor, in the case of continuous product discharge and at an average solids concentration in the reactor of more than 45% by weight, based on the total mass of the contents of the reactor, in the case of discontinuous product 20 discharge.

Furthermore, we have found a novel loop reactor for the polymerization of olefinic monomers which comprises a cyclic reactor tube and an axial pump, preferably an 25 impeller pump for conveying the polymerization mixture, wherein the diameter of the cyclic reactor tube varies by at least 10%, based on the predominant reactor tube diameter, and there is at least one widening and narrowing in a region other than that of the axial 30 pump.

BRIEF DESCRIPTION OF THE DRAWING

Figure 1 illustrates a process flow diagram of a loop reactor with varying diameter for olefin 35 polymerization.

The process of the present invention is suitable for polymerizing various olefinic monomers, in particular

for polymerizing ethylene, propylene and 1-butene or mixtures of these monomers. It is also possible to use additional monomers as comonomers, e.g. further α -olefins such as 1-pentene, 1-hexene, 1-octene or 1-decene.

Particular preference is given to a process in which ethylene is used as monomer and at least one α -olefin having from 3 to 8 carbon atoms, preferably 1-butene, 10 1-hexene or 1-octene, is used as comonomer. The amount of comonomer depends on the incorporation behavior of the particular catalyst in respect of the comonomer and on the desired density of the copolymer. The more comonomer incorporated into the polymer, the lower the 15 density of the copolymer will be. A person skilled in the art can readily set the monomer:comonomer ratio on the basis of these considerations.

If the catalyst permits, vinylaromatic comonomers such 20 as styrene or polar comonomers such as vinyl acetate, vinyl alcohols, acrylic acid or acrylic esters can also be polymerized. Cyclic monomers such as norbornene and dienes such as butadiene, 1,5-hexadiene or 1,7-octadiene are also possible as comonomers.

25 The polymerization process of the present invention can advantageously be carried out at from 20 to 150°C, preferably from 50 to 110°C, with an upper limit being imposed on the reaction temperature by the melting 30 point of the polymer to be formed.

The reaction pressure is usually in the range from 5 to 100 bar, preferably from 10 to 80 bar. Low pressures are generally associated with low space-time yields, 35 while higher pressures require an increased capital investment and lead to higher energy costs for compression. In general, a reaction pressure in the range from 20 to 50 bar represents a good compromise

between apparatus cost and reaction yield. When supercritical suspension media such as supercritical propane are employed, a higher pressure above the critical pressure can be appropriate from a technical
5 point of view.

Suitable suspension media for the process of the present invention are all media which are generally known for use in loop reactors. The suspension medium
10 should be inert and be liquid or supercritical under the reaction conditions and should have a boiling point which differs significantly from those of the monomers and comonomers used in order to make it possible to recover the starting materials from the product mixture
15 by distillation. Examples of customary suspension media are isobutane, butane, propane, isopentane, pentane and hexane.

An important feature of the process of the present
20 invention is that it allows polymerization at high ethylene concentrations. High proportions of solids in the reactor, in the present context also referred to simply as "reactor density", result in the proportion of the suspension medium in the reactor being correspondingly lower. In general, the smaller volume
25 of the suspension medium results in the amount of ethylene in the reactor also being lower, which leads to reduced polymer formation. In contrast, the process of the present invention makes it possible to increase
30 the ethylene concentration in the suspension medium and thus achieve higher polymer formation and a higher polymerization rate even at high reactor densities.

In a preferred embodiment of the process of the present
35 invention, the polymerization is therefore carried out at an ethylene concentration of at least 10 mol%, based on the suspension medium.

Thus, ethylene concentrations of 15 mol% and even 17 mol%, based on the suspension medium, were achieved in the process of the present invention.

5 In this context, the term "suspension medium" refers not simply to the suspension medium used, e.g. isobutane, but to the mixture of this suspension medium with the monomers dissolved therein. The ethylene concentration can be determined easily by gas-
10 chromatographic analysis of the suspension medium.

As mentioned at the outset, the technology of loop reactors has been known for a long time. In general, these reactors consist essentially of a cyclic reactor
15 tube having one or more ascending and one or more descending segments which are surrounded by cooling jackets for removing the heat of reaction and also horizontal tube sections which connect the vertical segments. The lower tube section usually accommodates
20 the axial pump, particularly the impeller pump, the feed facilities for catalyst and monomer and the discharge device, i.e. generally the sedimentation legs. However, the reactor can also have more than two vertical tube sections, so that a meandering
25 arrangement is obtained.

The present invention makes it possible to carry out a suspension polymerization process in a loop reactor at solids concentrations of more than 53% by weight, based
30 on the total mass of the contents of the reactor, and thus increase the production capacity of the loop reactor. These high solids concentrations can be achieved by various means.

35 In one embodiment of the present invention, the high solids concentration is achieved by the diameter of the cyclic reactor tube being varied by more than 10%, based on the predominant reactor tube diameter. A

widening of the reactor tube in the region of the axial pump necessitated by the construction should not be taken into consideration here, since such a widening serves primarily to accommodate the pump in the
5 reaction tube and highly turbulent flow prevails in this region in any case. Rather, the invention is based on the observation that, contrary to prevailing opinion, deliberate nonuniform flow of the polymerization mixture in the region of the reaction
10 tube even outside the region of the axial pump, particularly if an impeller pump is used, makes it possible to increase the solids concentration in the reactor. This effect appears, without wishing to be tied to this hypothesis, to be based on more effective
15 mixing of the heterogeneous reaction mixture. In particular, the monomer fed in, e.g. ethylene, is apparently dispersed more quickly in the reaction mixture, is dissolved more quickly in the suspension medium and is available to a greater degree for the
20 polymerization. The removal of the heat of reaction also appears to be aided, since the disturbance of the flow increases motion perpendicular to the flow direction, i.e. in the direction of the cooled reactor wall, which occurs to only a very limited extent in the
25 case of uniform plug flow.

To be able to influence the flow conditions in this desired way, the reaction tube diameter should be varied to a particular degree. The diameter of the tube
30 should vary by at least 10%, based on the predominant diameter of the reactor tube. For the present purposes, the predominant diameter of the reactor tube is the tube diameter which is constant over the longest stretch of the reactor tube. The tube diameter should
35 preferably vary by at least 20%, even better by at least 30% and very particularly preferably by at least 50%.

The conical widening of the reactor tube diameter in the flow direction should have a cone angle of about 0.5-10°, preferably 0.5-1.5°, and the cone angle at the narrowing of the tube diameter down to the predominant 5 tube diameter should be about 0.5-10°, preferably 1-3°.

The length of the sections having a widened tube diameter is preferably from 2 to 30 times the predominant tube diameter, particularly preferably from 10 5 to 15 times this tube diameter.

In a preferred embodiment of the process of the present invention, there is also an additional widening and narrowing of the reaction tube in the region of the 15 axial pump. As mentioned above, such widenings necessitated by the construction are already known. The effect of these widenings in accordance with the present invention can, however, be increased by making the widening greater and possibly also extending it 20 over a longer section of the tube than is required by the construction.

The effect of the present invention in terms of enabling the solids concentration in the reactor to be 25 increased appears to be based, inter alia, on better mixing of the monomer in the reaction mixture. It has been found that this inventive effect can be increased by feeding the monomer, i.e. for example ethylene, in at various points along the reaction tube. An 30 advantageous embodiment of the process of the present invention therefore comprises feeding at least one olefinic monomer in at least 2 points along the reactor tube. It has been found to be advantageous for the monomer to be fed in at, for example, 3 or 4 points 35 along the reactor tube. These feed points can be provided uniformly along the reactor tube, and it is advantageous for the feed points to be located in each case upstream of the widenings of the tube, but not in

the region of the last vertical segment before the product discharge region.

To further increase the solids concentration in the
5 reactor in a preferred embodiment of the present invention the reactor may have one or more by-pass lines connecting two points of the main loop by an alternate route having a different transit time than that of the main route and/or a modified axial pump
10 with internal recirculation and/or a mixing element that improves the homogeneity of the circulation slurry, as described in WO 04/26463.

It is known from US-A-6,239,235 that a continuous
15 discharge system can also be useful for increasing the solids concentration in the reactor. This measure can be combined with the process of the present invention. Accordingly, the present invention also provides a process as described above in which the polymer formed
20 is discharged continuously from the reactor.

The high solids concentration in the reactor which is sought according to the present invention can, as indicated above, be achieved by the abovementioned
25 means. Particular preference is given to a process in which the polymerization is carried out at an average solids concentration in the reactor of more than 53% by weight, based on the total mass of the contents of the reactor. This solids concentration is preferably above
30 55% by weight, more preferably above 58% by weight and particularly preferably above 60% by weight. As shown in the examples, solids concentrations of more than 62% by weight can be achieved. For the present purposes, the average solids concentration is then the solids
35 concentration in the reaction tube. Even higher solids concentrations can be observed in the discharge system, whether continuous or discontinuous, due to sedimentation.

The high solids concentrations can be achieved by the measures provided by the present invention even without continuous discharge of the polymer product. One 5 variant of the process of the present invention therefore comprises discharging the polymer formed from the reactor in a discontinuous fashion and carrying out the polymerization at an average solids concentration in the reactor of more than 45% by weight, based on the 10 total mass of the contents of the reactor. Under these conditions, the solids concentration in the reactor is preferably above 50% by weight, particularly preferably above 55% by weight.

15 The process of the present invention can be operated as a single-stage process, but can also be carried out as a multistage cascade process by combining it with further polymerization reactors. One embodiment of the process of the present invention is therefore a process 20 for polymerizing at least one olefinic monomer in a loop reactor, wherein the polymerization in this loop reactor is preceded or followed by at least one further polymerization step in a loop reactor or a gas-phase reactor. Such cascade processes, albeit without the 25 specific features of the present invention, are described, for example, in EP-A-517 868 and US-A-6 355 741.

Apart from the above-described disturbance of the 30 suspension flow in the reaction tube, the reactor density can also be influenced by other measures, for example by selection of a particularly suitable catalyst.

35 Catalysts suitable for use in the process of the present invention are in principle all catalysts which are also used otherwise in loop reactors, i.e., for example, chromium catalysts of the Phillips type,

Ziegler catalysts, Ziegler-Natta catalysts or single-site catalysts such as metallocene catalysts. Phillips catalysts have become particularly widespread in loop reactors, and can also be used particularly advantageously in the process of the present invention. Among these catalysts, particular preference is given to those described in the patent applications WO-01/18069, WO-01/17675, WO-01/17676 and WO-01/90204.

The invention also provides a loop reactor for the polymerization of olefinic monomers which comprises a cyclic reactor tube and an axial pump, particularly an impeller pump for conveying the polymerization mixture, wherein the diameter of the cyclic reactor tube varies by at least 10%, based on the predominant reactor tube diameter, and there is at least one widening and narrowing in a region other than that of the axial pump. Particular preference is in turn given to a loop reactor in which facilities for feeding monomers into the reactor tube are located at at least 2 points.

Figure 1 illustrates the elements of the reactor of the present invention. The figure shows a reactor according to the present invention having two ascending (1) and two descending segments (2) which are joined to one another by bends. Ethylene is fed via the lines (3) to the suspension medium inlets (4) and thus enters the reactor, in the present case at two points. The polymeric product settles in the sedimentation legs (5) and is from there discharged discontinuously from the reactor. The reaction suspension is circulated and mixed by the impeller (6). The regions (7) indicate regions having a widened tube diameter, and region (8) indicates a region having the predominant tube diameter.

Example

The preparation of the catalyst up to the activation step was carried out by the method described in WO 01/90204. Activation was then carried out at 650°C in the presence of air in a fluidized-bed activator.

5 Fluoride doping was carried out by use of a mixture of the catalyst precursor with 2.5% by weight of ammonium hexafluorosilicate (resulted in a fluoride content of about 1% by weight, based on the total mass of the catalyst) in the activation. For activation, this

10 mixture was heated to 350°C over a period of 1 hour, maintained at this temperature for 1 hour, subsequently heated to the desired activation temperature of 650°C, maintained at this temperature for 2 hours and subsequently cooled, with cooling below 350°C being

15 carried out under N₂.

Polymerization:

Ethylene was copolymerized with 1-hexene at 104°C and a pressure of 39 bar using the above-described catalyst in a loop reactor having a reactor volume of 0.18 m³ and the geometry shown in Figure 1. Ethylene was fed into the reactor at two points, one shortly before the impeller. Isobutane was used as suspension medium. The isobutane was fed into the reactor at 6 points, including in the region of the impeller pump shaft and the place where the catalyst was introduced. The impeller pump was operated at 1700-1900 revolutions per minute. The product was discharged discontinuously via customary sedimentation legs. Polymerizations were carried out at slightly different ethylene/isobutane ratios, but the resulting product always had a density of about 0.949 g/ccm and a high-load melt index (21.6/190) of about 6.0. A reactor density of above 62% by weight, based on the total mass of the contents of the reactor, was achieved.

We claim:

1. A process for polymerizing at least one olefinic monomer in a loop reactor at from 20 to 150°C, but
5 below the melting point of the polymer to be formed, and a pressure of from 5 to 100 bar, where the polymer formed is present in a suspension in a liquid or supercritical suspension medium and this suspension is circulated by means of an axial
10 pump, wherein the loop reactor comprises a cyclic reactor tube whose diameter varies by at least 10%, based on the predominant reactor tube diameter, and in which there is at least one widening and narrowing in a region other than that
15 of the axial pump.
2. A polymerization process as claimed in claim 1, wherein the polymerization is carried out at an average solids concentration in the reactor of more than 53% by weight, based on the total mass of the contents of the reactor, in the case of continuous product discharge and at an average solids concentration in the reactor of more than 45% by weight, based on the total mass of the contents of the reactor, in the case of discontinuous product discharge.
20
3. A process as claimed in claim 1 or 2, wherein there is an additional widening and narrowing of the reactor tube in the region of the axial pump.
30
4. A process as claimed in any of the preceding claims, wherein ethylene is used as monomer and at least one α-olefin having from 3 to 8 carbon atoms is used as comonomer.
35
5. A process as claimed in any of the preceding claims, wherein at least one olefinic monomer is

fed in at at least 2 points along the reactor tube.

6. A process as claimed in any of the preceding claims, wherein the polymer formed is discharged continuously from the reactor.
7. A process as claimed in any of the preceding claims, wherein the polymerization is carried out at an ethylene concentration of at least 10 mol%, based on the suspension medium.
8. A process for polymerizing at least one olefinic monomer in a loop reactor as claimed in any of the preceding claims, wherein the polymerization in this loop reactor is preceded or followed by at least one further polymerization step in a loop reactor or a gas-phase reactor.
9. A loop reactor for the polymerization of olefinic monomers which comprises a cyclic reactor tube and an axial pump for conveying the polymerization mixture, wherein the diameter of the cyclic reactor tube varies by at least 10%, based on the predominant reactor tube diameter, and there is at least one widening and narrowing in a region other than that of the axial pump.
10. A loop reactor as claimed in claim 9, wherein facilities for feeding monomers into the reactor tube are located at at least 2 points.

Abstract

Process for polymerizing at least one olefinic monomer in a loop reactor at from 20 to 150°C, but below the 5 melting point of the polymer to be formed, and a pressure of from 5 to 100 bar, where the polymer formed is present in a suspension in a liquid or supercritical suspension medium and this suspension is circulated by means of an axial pump, wherein the loop reactor 10 comprises a cyclic reactor tube whose diameter varies by at least 10%, based on the predominant reactor tube diameter, and in which there is at least one widening and narrowing in a region other than that of the axial pump.

